

# Direct $k$ -space mapping of the electronic structure in an oxide-oxide interface

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The interface between  $\text{LaAlO}_3$  and  $\text{SrTiO}_3$  hosts a two-dimensional electron system of *itinerant* carriers, although both oxides are band insulators. Interface ferromagnetism coexisting with superconductivity has been found and attributed to *local* moments. Experimentally, it has been established that Ti  $3d$  electrons are confined to the interface. Using soft x-ray angle-resolved resonant photoelectron spectroscopy we have directly mapped the interface states in  $k$ -space. Our data demonstrate a charge dichotomy. A mobile fraction contributes to Fermi surface sheets, whereas a localized portion at higher binding energies we tentatively attribute to electrons trapped by O-vacancies in the  $\text{SrTiO}_3$ . While photovoltage effects in the polar  $\text{LaAlO}_3$  layers cannot be excluded, the apparent absence of *surface-related* Fermi surface sheets could also be fully reconciled in a recently proposed electronic reconstruction picture where the built-in potential in the  $\text{LaAlO}_3$  is compensated by *surface* O-vacancies serving also as charge reservoir.

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Breaking the translational or inversion symmetry at surfaces and interfaces may lead to a rearrangement of charge, spin, orbital, and lattice degrees of freedom. The consequences are particularly interesting in the case of oxides since there already a slight shift in the balance of the respective interactions can stabilize one out of several competing orders or even create novel phases. A case in point is the formation of a high-mobility two-dimensional electron system (2DES) from Ti  $3d$  states at the interface of  $\text{LaAlO}_3/\text{SrTiO}_3$  (LAO/STO) heterostructures [1–9] which undergoes a transition into a two-dimensional superconducting state below 0.2 K [4]. However, depending on growth conditions LAO/STO has also been found to display pronounced magnetotransport effects indicating the existence of local moments [10]. More recently, even the simultaneous presence of ferromagnetism and superconductivity has been reported, possibly due to phase separation within the interface [11–14].

The physical origin of the 2DES formation is still debated. The observation that both interface conductivity as well as ferromagnetism only appear for a critical LAO thickness of 4 unit cells (uc) and beyond has been related to electronic reconstruction [2, 13]. In this scenario electrons are transferred from the surface to the interface in order to minimize the electrostatic energy resulting from the polar discontinuity between LAO and STO [3]. Alternative explanations involve doping by oxygen vacancies [10] and/or cation intermixing [15] but so far have

failed to account for the critical thickness. What hampers a better understanding is the lack of microscopic information, in particular on the electronic properties of the interface and the adjacent oxide layers.

Photoelectron spectroscopy is unique in that it can directly probe the single-particle excitations of the valence electrons, which determine the low-energy properties of a solid. Regarding the Ti  $3d$  interface electrons in LAO/STO, however, this is hindered for conventional photon energies in the range of 20–100 eV by the insufficient probing depth while in the hard x-ray regime the photoabsorption cross-sections are too low. Only recently, it has been shown that the Ti  $3d$  states nevertheless can be detected by exploiting the resonance enhancement at the Ti  $L$  edge, i.e. by utilizing soft x-rays [8, 9]. Here we use soft x-ray resonant photoelectron spectroscopy (SX-ResPES) to probe the occupied part of the electronic states and in particular its angle-resolved (AR) mode to record Fermi surface (FS) and band maps. Note that the resulting electronic structure may differ from that probed in transport measurements due the additional presence of x-ray induced photocarriers [6, 16].

The LAO/STO heterostructure with a 4 uc thick LAO overlayer was grown at the University of Augsburg by pulsed laser deposition on a  $\text{TiO}_2$ -terminated STO substrate. The film thickness was monitored by reflection high-energy electron diffraction (RHEED). During growth the oxygen pressure amounted to  $1 \times 10^{-4}$  mbar

while the substrate was held at 780 °C. Subsequently, the sample was cooled down to room temperature in 0.4 bar of oxygen. Prior to the measurements, the sample surface was cleaned by ozone and gentle *in situ* heating at 180° (for details see Supplementary Information).

The experiments were performed at the soft X-ray beamline BL23SU of SPring-8 using a photoemission spectrometer equipped with a Gammadata-Scienta SES-2002 electron analyzer [17] and the fully circularly polarized light from a helical undulator. The energy resolution was set to 110 meV for the angle-integrated and 180 meV for the angle-resolved experiments while the sample temperature was 20 K for all measurements. The angular resolution of the SX-ARPES measurements was 0.2° along and 0.5° perpendicular to the analyzer slit. The Fermi surface map was generated by integrating energy distribution curves at each  $k$ -point over an interval of 0.3 eV centered around the Fermi energy. All spectra were corrected for the contribution from second order light (see Supplementary Information). The position of the Fermi level was determined from an *in situ* evaporated gold film.

The density functional calculations have been performed using the generalized gradient approximation (GGA+ $U$ ) in the Perdew-Burke-Ernzerhof pseudopotential implementation [19] in the QUANTUM ESPRESSO (QE) package [20], with the local Coulomb repulsion  $U$  between Ti 3d electrons being 2 eV (for details see Supplementary Information).

In Fig. 1(a) we show angle-integrated ResPES spectra near the chemical potential for a sample with a conducting interface (4uc LAO) upon tuning the photon energy through the Ti  $L$  absorption edge (for details on ResPES see Supplementary Information). The complete valence band spectrum, measured on resonance ( $h\nu=460.20$  eV), is depicted in Fig. 1(c). The off-resonance spectrum ( $h\nu=445.95$  eV) shows no spectral weight at the chemical potential. Moving through the resonance two structures appear — indicating that both are of Ti 3d character —, a broad structure at a binding energy of  $\approx 1.3$  eV ( $A$ ) and a structure which is cut off by the Fermi-Dirac distribution function (exemplarily marked by  $B$  in the spectrum recorded at  $h\nu=460.20$  eV) and hence is tentatively ascribed to metallic states. Interestingly, the two features  $A$  and  $B$  resonate at different photon energies which already signals that they originate from different types of electronic states.

To get further insight, one has to relate the ResPES excitation energies to their positions on the resonance curve, i.e. the x-ray absorption spectrum [Fig. 1(b)]. The spectrum to compare with is that of a reference sample representative for Ti in a 3+ oxidation state, here  $\text{LaTiO}_3$  (green), while for LAO/STO (red) the absorption is dominated by the  $\text{Ti}^{4+}$  ions of the substrate. Peak  $A$  resonates exactly on the absorption maximum (associated with the so-called  $e_g$  levels) of  $\text{LaTiO}_3$  ( $\text{Ti}^{3+}$ ) whereas the enhancement of  $B$  is delayed by  $\approx 1$  eV to almost the fol-

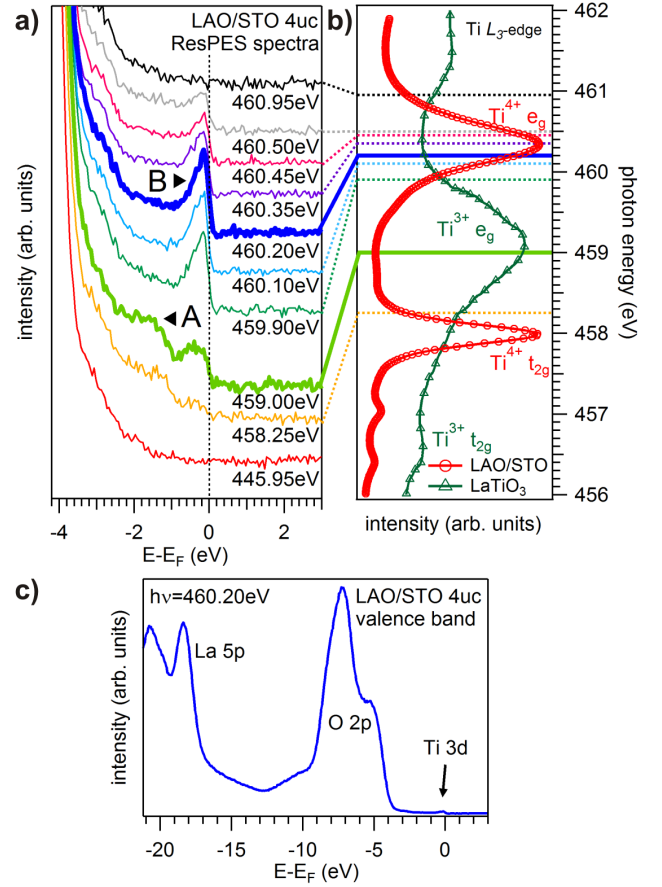


FIG. 1. (Color online) (a) Angle-integrated resonant photoemission spectra upon tuning the photon energy through the Ti  $L$  absorption edge. (b) Ti  $L$  absorption spectra, recorded in total electron yield mode, of LAO/STO (red) and  $\text{LaTiO}_3$  (green, taken from Ref. [7]). The photon energies used in the measurements displayed in (a) are indicated by dashed and solid lines. (c) On-resonance photoemission spectrum, displaying the complete valence band.

lowing minimum. A sharp resonance at the maximum is expected for absorption into localized atomic-like states, whereas a delayed resonance can be understood as originating from concomitant interband transitions between delocalized Bloch states [21]. Therefore, we attribute feature  $A$  to localized electrons in impurity states of Ti 3d character, probably surrounding and being trapped at oxygen vacancies. Our recent band structure calculations based on density-functional theory (DFT) reveal similar peaks in the density of states between  $-2$  eV and  $-1$  eV, depending on O vacancy configuration and concentration [14]. Similar observations have been reported for PES experiments on bare STO surfaces [22, 23], where the spectral weight at the chemical potential and the in-gap states around  $-1.3$  eV were discussed in terms of coherently screened and poorly screened excitations [23], respectively.

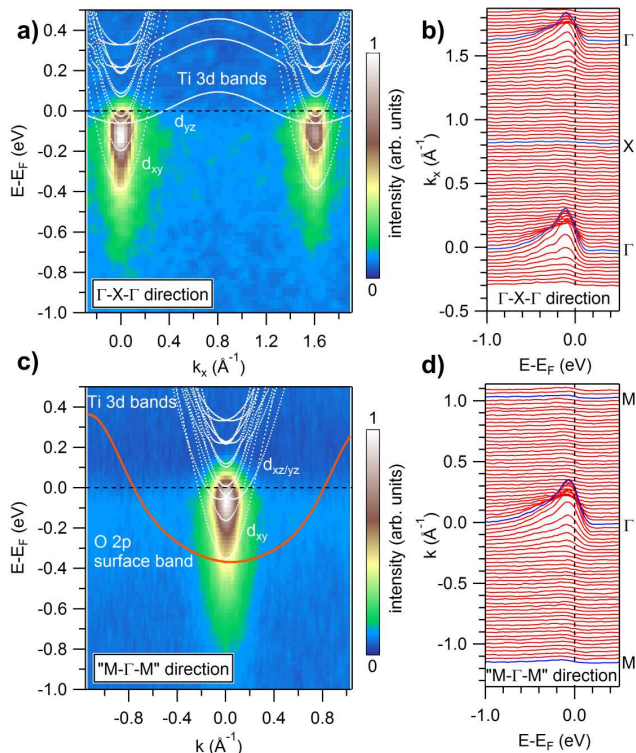


FIG. 2. (Color online) (a) Band map along the  $\Gamma$ -X- $\Gamma$  line of the BZ. (b) Same data as in (a) depicted as energy distribution curves. (c) Band map along a cut close to the M- $\Gamma$ -M line of the BZ (hence denoted by "M- $\Gamma$ -M"). (d) Same data as in (c), depicted as energy distribution curves. All data were taken at  $h\nu = 460.20$  eV.

Since momentum information is still preserved in valence band photoemission using soft x-rays and due to the resonance enhancement at the Ti  $L$  edge we have been able to perform  $k$ -space mapping of the 2DES interface states. In Figs. 2(b) and (d) we display  $k$ -resolved PES spectra along the  $\Gamma$ -X- $\Gamma$  direction and a cut close to the M- $\Gamma$ -M line [see dashed lines in Fig. 3(b)]. One clearly observes states dispersing with  $k$  around  $\Gamma$  and an occupied band width of  $\approx 0.4$  eV, conclusively confirming our tentative assignment from above to the metallic interface band states of the 2DES. The same data is depicted as band maps in Figs. 2(a) and (c), with the electronic dispersions of DFT calculations overlaid. The calculations fairly reproduce the experimental band width, while the experimental broadening does not allow us to resolve all the individual quantum well states owing to the confinement of the 2DES [24], although the energy distribution curves in Figs. 2(b) and (d) indicate the existence of at least two bands.

Additional information can be extracted from the FS map in Fig. 3. An essentially isotropic distribution of high intensity centered at the  $\Gamma$  points of the BZ of STO is observed. Superimposed one finds, with much lower intensity, flower-shaped spectral weight with the lobes

directed towards the X points of the BZ and stretching further out than the isotropic intensity distribution as is most clearly seen around the lower left  $\Gamma$  point in Fig. 3(a). These observations are in line with the FS sheets from the DFT calculations which are overlaid on top of the PES data in Fig. 3(b). Note however that the experimental Fermi surface volume might be slightly enhanced due to photo-generated charge carriers [6]. The calculations further reveal that the isotropic intensity distribution originates mainly from light Ti  $3d_{xy}$  bands while the flower-shaped intensity distribution is due to heavy  $d_{xz}/d_{yz}$  bands, similar to what has recently been reported for a 2DES at the surface of bare STO [24].

However, there is also a striking discrepancy between experiment and theory. In the calculations, which are performed for stoichiometric samples, i.e., in the absence of oxygen vacancies in the LAO, a hole-like FS is predicted around the M points as indicated by the orange dashed lines in Fig. 3(b). It is due to the Fermi level crossing of O  $2p$  derived states from the valence band maximum of the topmost monolayer of the LAO film. Since the photoelectron current emitted from the surface is hardly damped by scattering events and since the band is almost completely filled, these hole pockets, if existing, should be observable even without resonance enhancement. In the standard electronic reconstruction scenario [Fig. 4(a)] the polarity-induced potential build-up across the overlayer gradually shifts the valence band of LAO towards the Fermi level. At the critical thickness, the valence band maximum crosses the Fermi level which gives rise to the hole pockets predicted by the DFT calculations, while the released electrons populate the lowest lying Ti  $3d$  states at the STO side of the interface [25].

From the obvious absence of metallic surface bands we conclude that the potential difference is screened out in the LAO film. A possible explanation could be that under illumination electron-hole pairs are created which get separated by the initial polarization field in the LAO [Fig. 4(b)]. Eventually, depending on the rates for electron-hole pair creation and recombination a dynamic equilibrium will be established where the opposing electric field due to the separated electron-hole pairs just cancels the initial field. On the other hand, in another polar/non-polar heterostructure (LaCrO<sub>3</sub>/SrTiO<sub>3</sub>) a built-in potential has readily been identified by x-ray photoelectron spectroscopy (XPS) with a similar potential drop per uc as expected for LAO/STO in the standard electronic reconstruction scenario [26].

Looking for alternative explanations, our SX-ARPES results could also be fully reconciled within recent proposals, also based on DFT calculations, that oxygen vacancies that form at the LAO surface can serve as charge reservoir for the electronic reconstruction [27–30]. In such a scenario the O vacancies induce unoccupied in-gap states, which due to possible disorder of the vacancies in the real system might easily become localized. The re-



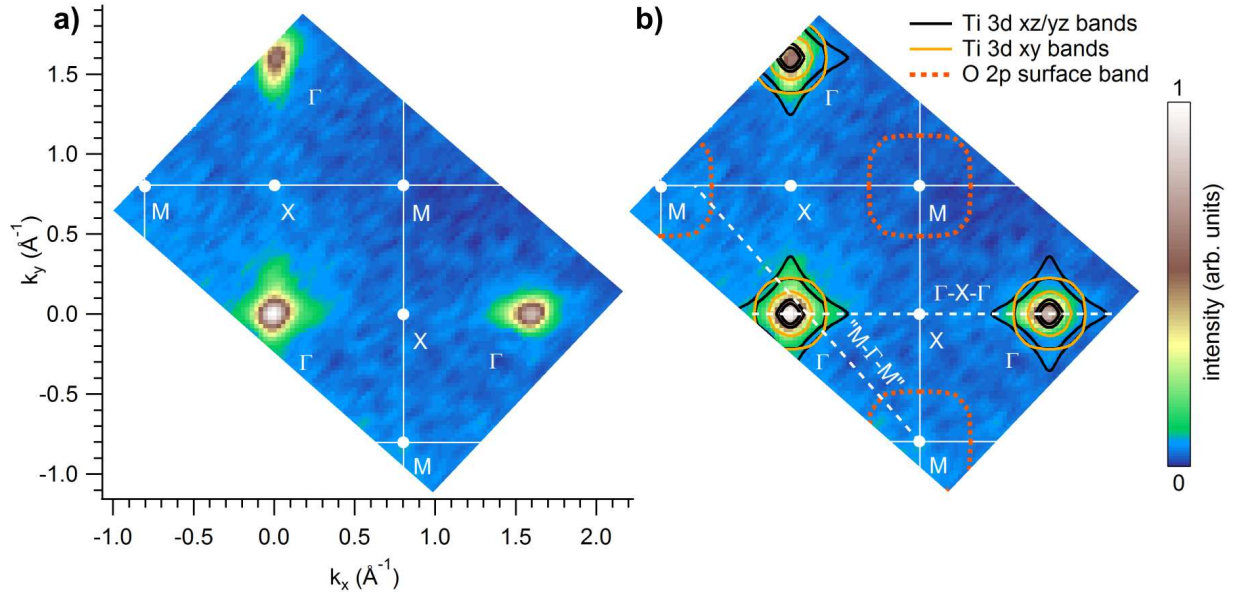


FIG. 3. (Color online) (a) FS map recorded at  $h\nu = 460.20$  eV. (b) Same map as (a) but with the cuts in the BZ corresponding to the data in Fig. 2(a)-(d) indicated and the FS sheets from DFT calculations overlaid.

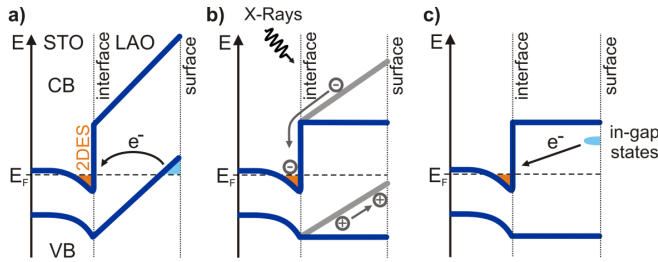


FIG. 4. (Color online) (a) Schematic band diagram for the standard electronic reconstruction scenario in LAO/STO. (b) Possible situation where the polarization field in the LAO is screened by the separation of electron-hole pairs created upon illumination with x-rays. (c) Tentative band diagram with the inclusion of O vacancies at the LAO surface as charge reservoir for electronic reconstruction.

leased two electrons per O vacancy are transferred to the interface by the LAO polar field. This field is thereby efficiently reduced [see Fig. 4(c)], in line with XPS measurements which show no core-level broadening or shift with film thickness [31]. In this particular case electronic reconstruction sets in at a critical thickness when the energy gain of screening the built-in potential by transferring two electrons exceeds the formation energy of an O vacancy. However, any mechanism where the charge transferred to the interface is not released from the LAO valence band maximum shifted across the band gap up to the Fermi energy but from trapped in-gap states would be compatible with our data.

Our data provide evidence that at the conducting in-

terface besides heavy Ti  $3d_{xz/yz}$  and light Ti  $3d_{xy}$  bands there also exist *localized* charge carriers of Ti 3d character. These are probably trapped by adjacent O vacancies, i.e. O vacancies in the STO at the interface. It is hence tempting to associate the trapped and mobile interface charge with ferromagnetism and superconductivity, respectively [14], which both have recently been reported to coexist at the interface. As a matter of fact, the hallmarks of the microscopic view of the standard electronic reconstruction scenario — a metallic surface and a potential drop across the LAO overlayer of the order of the STO band gap — experimentally remained elusive so far. Our data clearly indicate that they are absent in our spectroscopic experiments. Modified electronic reconstruction scenarios involving surface O vacancies as charge reservoir could explain these findings. Since we cannot rule out the possibility that the LAO polar field is screened out by a photoinduced reverse voltage our results call for both a systematic investigation of scenarios taking O vacancies into account and combined *in situ* transport and spectroscopy experiments. In any case, these results demonstrate for the first time that SX-ARPES can provide valuable  $k$ -space information on the electronic structure of *buried* interfaces.

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## SUPPLEMENTAL INFORMATION

### RESONANT PHOTOELECTRON SPECTROSCOPY (RESPES) – TECHNIQUE AND DATA NORMALIZATION

Photoemission (PES) from the Ti  $3d$  interface states can only be accomplished with reasonable intensity, if one takes advantage of the resonance enhancement at the Ti  $L$  absorption edge. With the photon energy tuned to the absorption threshold, a second path opens how to arrive at the same final state as in the direct photoemission process [Fig. 5(a)]:

$$2p^6 3d^n \rightarrow 2p^6 3d^{n-1} + \epsilon \quad (\text{direct PES}), \quad (1)$$

$$2p^6 3d^n \rightarrow 2p^5 3d^{n+1} \rightarrow 2p^6 3d^{n-1} + \epsilon \quad (\text{Auger decay}), \quad (2)$$

where  $\epsilon$  denotes the ejected photoelectron. This second path involves the dipole excitation of an electron from the Ti  $2p$  into the Ti  $3d$  shell and a subsequent Auger-like decay (often called direct recombination), resulting in the ejection of a  $3d$  electron and a filled  $2p$  shell. The probability amplitudes of both channels interfere quantum mechanically and give rise to a resonance enhancement of only the  $3d$  spectral weight [1].

All spectra were normalized in intensity to the non-resonating La  $5p$  core-level intensity at  $-18.4\text{ eV}$  [see Fig. 5(b)]. The energy scale was calibrated at the Fermi level observed in the LAO/STO spectra.

### CORRECTION FOR 2<sup>nd</sup> ORDER CONTRIBUTIONS

Significant intensity from the Ti  $2p_{3/2}$  core level excited by 2<sup>nd</sup> order light appeared in all spectra in the region around the chemical potential [see Fig. 6(a)] although the 2<sup>nd</sup> order light is much weaker than the intensity of the 1<sup>st</sup> harmonic. For spectra measured at photon energies between  $459.90\text{ eV}$  and  $460.95\text{ eV}$  the 2<sup>nd</sup> order light induced peak was fitted by a Gaussian line and subtracted from both the angle-integrated and angle-resolved spectra.

For the spectra measured at lower photon energies ( $445.95\text{ eV}$ ,  $458.25\text{ eV}$  and  $459.00\text{ eV}$ ) the 2<sup>nd</sup> order peak overlaps with 1<sup>st</sup> order spectral weight below the chemical potential. It was subtracted by using the Gaussian lineshape observed at higher photon energies and accounting for the  $2\Delta h\nu$  shift of second order light, if the fundamental photon energy changes by  $\Delta h\nu$ . The

second order excitation of the Ti  $2p$  electrons also allowed for an absolute calibration of the photon energies used in photoemission and x-ray absorption.

### SAMPLE SURFACE PREPARATION

For the measurements a clean sample surface is essential to minimize scattering of the photoelectrons and optimize the signal-to-noise ratio of the spectra. The sample was transported under air to the synchrotron. Prior to the measurements the sample was kept under ozone flow for 45 min, followed by an *in situ* annealing at  $180^\circ\text{C}$  under  $1 \times 10^{-5}\text{ mbar}$  of oxygen for 45 min. After this procedure a high quality LEED pattern with a  $1 \times 1$  surface is observed [see Fig. 6(b)], signalling a clean and long-range ordered LAO surface. The lattice constant inferred from this pattern is  $(3.97 \pm 0.1)\text{ \AA}$ , which is within the error bars in good agreement with the lattice constant of STO ( $3.905\text{ \AA}$ ). No surface reconstruction was found.

### DENSITY FUNCTIONAL CALCULATIONS

Density functional calculations have been performed using the generalized gradient approximation (GGA+ $U$ ) in the Perdew-Burke-Ernzerhof pseudopotential implementation [2] in the QUANTUM ESPRESSO (QE) package [3]. The local Coulomb repulsion  $U$  between Ti  $3d$  electrons was chosen to be  $2\text{ eV}$ .

A number of supercells consisting of two symmetric LAO/STO parts were generated, where each part contains a stack of 4 uc thick LAO layers on a 3.5 uc thick STO slab. The interfacial configuration is considered as  $\text{TiO}_2/\text{LaO}$ . The LAO-STO-LAO parts are separated by a  $13\text{ \AA}$ -thick vacuum sheet. A kinetic energy cutoff of  $640\text{ eV}$  and the Brillouin zone (BZ) of the 106-to 166-atom supercells sampled with  $5 \times 5 \times 1$  to  $9 \times 9 \times 1$   $k$ -point grids are used. For the stoichiometric vacancy-free structures, the electronic state can be characterized as metallic, with the interface electron charge emerging due to the compensation of the polar field across the LAO. The number of electrons per  $(1 \times 1)$  uc transferred to the  $t_{2g}$  states of the  $\text{TiO}_2$ -layers at the interface amounts to 0.34.

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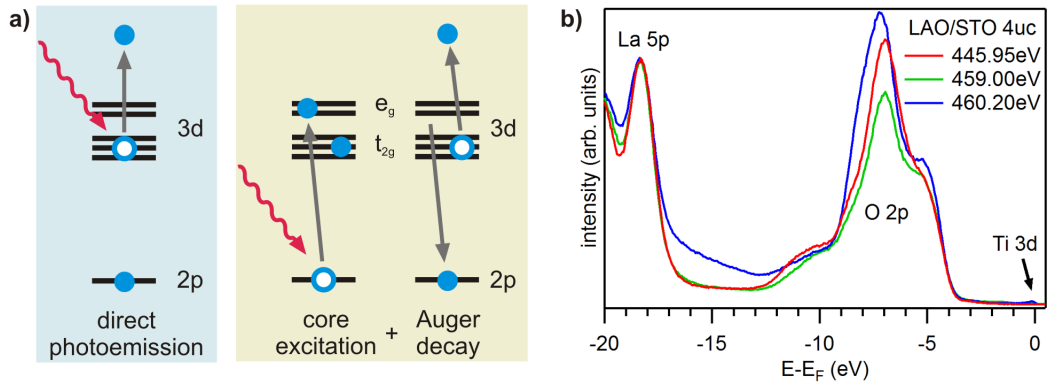


FIG. 5. (Color online) Resonant enhancement in photoemission and data normalization. (a) Sketch of the two excitation channels which quantum mechanically interfere in resonant photoemission. (b) The spectra have been normalized to the non-resonating La 5p core-level as is shown here for spectra measured at  $h\nu = 445.95$  eV (off-resonance),  $h\nu = 459.00$  eV ( $\text{Ti}^{3+}$   $e_g$  resonance), and  $h\nu = 460.20$  eV (on-resonance for Fermi surface mapping).

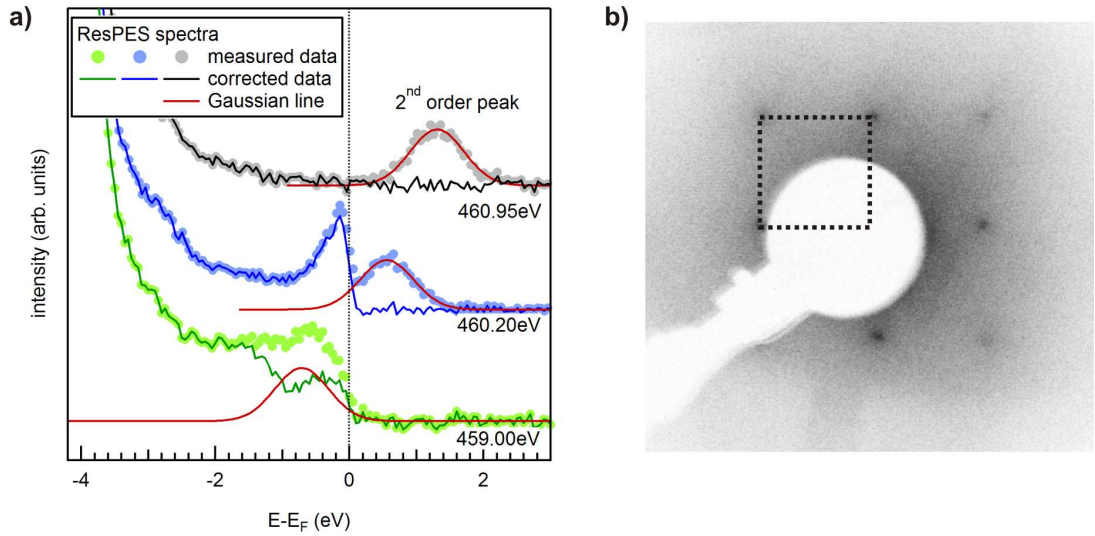


FIG. 6. (Color online) (a) Correction of the 2<sup>nd</sup> order light induced peak by subtraction of a Gaussian, exemplarily shown for spectra measured at 459.00 eV, 460.20 eV and 460.95 eV. (b) LEED pattern of a surface-cleaned LAO/STO sample at  $E = 128.1$  eV showing a  $1 \times 1$  surface structure. The lattice constant is 3.97 Å.